

## Preparation of Self Assembled Monolayer of Thiol in Aqueous Solutions

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Among the various molecule-substrate pairs in chemisorbed ordered-monolayers, n-alkanethiols adsorbed on to gold are a most popular combination. Those monolayers had been deposited by spontaneous adsorption from ethanolic solutions. In this study, a preparation of self assembled monolayer of n-alkanethiol on to gold was investigated in aqueous solutions.

Substrate electrodes were immersed in 0.05 M KOH aqueous solutions containing n-alkanethiol. The electrode potential was kept constant during the formation of self-assembled monolayers (SAM). Monolayers formed at gold electrode surfaces by our method were characterized by cyclic voltammetry, electrochemical quartz crystal microbalance (EQCM), and scanning atomic force microscopy (AFM).

BAS No. 010310 polycrystalline gold disk with diameter of 1.6mm, Mateck single crystalline gold (111) disk with diameter of 8mm, and BAS EQCM gold electrode were used as substrate electrodes.

The gold electrodes were subjected to the treatment procedure before each experiment. Cyclic voltammetry was used to reconstitute the surface, obtaining almost identical voltammograms in deaerated 0.05 M KOH solutions, within the -0.400 to -1.400 V potential range vs. Ag|AgCl. The polycrystalline gold electrode was polished with alumina slurry prior to the cyclic voltammetric treatment.

For monolayer studies, thus treated electrode upon return from the positive scan, were removed from the solution, rinse with water and immersed in 0.05 M KOH solution containing  $5 \times 10^{-5}$  M n-alkanethiol. The deposition was carried out at -0.2 V vs. Ag|AgCl for 20~30 minutes. Ar was bubbled through the solution during the deposition process.

The integrity of self-assembled n-alkanethiols ( $\text{CH}_3(\text{CH}_2)_n\text{SH}$ ,  $n=3, 5, 7, 9$ ) monolayer prepared by our method on polycrystalline gold electrodes was tested by means of the cyclic voltammetry technique in the presence of potassium ferrocyanide. The electrode reaction of ferrocyanide on the gold electrodes covered with SAM of thiol was completely suppressed even when butanethiol was used as an adsorbate. The integrity of adsorbed film was improved furthermore by the heat treatment in boiling water.

The double layer capacities of the polycrystalline gold electrode covered with SAM of thiol were also measured by means of residual current of cyclic voltammograms. The values obtained were considerably large than the values reported for SAM of thiol deposited from ethanolic solutions. The heat treatment in boiling water reduced the double layer capacity of the SAM of thiol prepared in this study.

The cyclic voltammetry for the reductive desorption was used to estimate the quantities of adsorbed thiols. The adsorbed amounts of thiol molecules were calculated from the area under the peak, assuming the one-electron reduction and neglecting the contribution of charging current. The values thus obtained for decanethiol were  $1.6 \times 10^{-9}$ ,  $1.5 \times 10^{-9}$ ,

and  $1.4 \times 10^{-9}$  mol  $\text{cm}^{-2}$  for polycrystalline gold electrode, EQCM gold electrode, and for single-crystalline Au (111) electrode respectively. Those values are greater than the theoretical values for Au (111),  $7.5 \times 10^{-10}$  mol  $\text{cm}^{-2}$ . The discrepancies are likely to be attributable to the difference in gold surface plane and to the double layer charging upon desorption.

The self-assembly process was found to undergo inhibition by coexistence substances such as sodium sulfate and polyoxyethylenelauryether (LEO). The inhibition of self-assembly process was investigated by chronopotentiometry for the reaction of ferrocyanide on the gold electrodes covered with SAM of thiol. The extent of the inhibition was found to depend on the applied potential. The inhibition effect became minimum at -0.2 V vs. Ag|AgCl where is equivalent to the zero charge potential of gold electrodes. Those findings show that the inhibition is due to the adsorption of coexistence species.

The mass change at the gold electrode surface-electrolyte solution interface was measured by an electrochemical quartz crystal microbalance (EQCM). The increase in mass during the self-assembly process in 0.05 M KOH aqueous solution under the constant potential reached plateau with the mass equivalent to a monolayer film. The reductive desorption of SAM of thiol in 0.05 M KOH aqueous solutions was measured by cyclic voltammetry with EQCM. The mass at the electrode surface-electrolyte solution interface was increased during the first reduction cycle. The observed mass change was equivalent to one potassium ion per thiol molecule. The result shows that the SAM of thiol prepared in this study does not directly desorbed in the initial stage even if it was reduced, but generate an ion pair with potassium ion.

In AFM study, the conventional  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure was observed on some area of adsorbed films. A morphological change was observed after the heat treatment in boiling water.